201-14298A

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## ROBUST SUMMARY FOR CRUDE BHMT

Summary

Crude BHMT is the high-boiling fraction from the distillation of hexamethylene diamine. Because it is the residue of a distillation and the processing times and conditions are adjusted to maximize the yield of hexamethylene diamine, it is an inconsistent mixture. Crude BHMT is also known as:

BHMT Amine;
Amines Bottoms;
CAS NO 68411-90-5;
Hexanedinitrile, hydrogenated, high-boiling fraction; and
Adiponitrile, reaction product with hydrogen, high-boiling fraction;

It has a variable composition (dry weight basis) of ~50-70% bis-hexylmethylenetriamine (BHMT), ~20-35% oligomeric amines, ~0-10% $C_{10}$ amines, ~0-10% hexamethylenediamine, ~0-10% caprolactam, ~0-5% adiponitrile, and ~0-5% 6-aminocapronitrile, and small amounts of related compounds.

Available data are presented in this document on crude BHMT and purified BHMT (the main component of the mixture).

| Chemical Name | CAS Registry Number | Structure |
|---|---|---|
| Crude BHMT | 68411-90-5 | Variable mixture |
| BHMT | 143-23-7 | $H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$ |

The scientific literature was searched and summarized (Table 1). Studies were obtained and evaluated for adequacy. Robust summaries were developed for adequate studies addressing specific SIDS endpoints. Summaries were also developed for studies either considered not adequate but provided information of relevance for hazard identification and evaluation, or covered non-SIDS endpoints (Appendices A and B).

**Table 1: Matrix of Available and Adequate Data on Crude BHMT and BHMT**

| | Crude BHMT | BHMT |
|---|---|---|
| **PHYSICAL/CHEMICAL CHARACTERISTICS** | | |
| Melting Point | √ | √ |
| Boiling Point | √ | √ |
| Vapor Pressure | √ | √ |
| Partition Coefficient (Log Kow) | –/* | √ |
| Water Solubility | √ | √ |
| **ENVIRONMENTAL FATE** | | |
| Photodegradation | √ | √ |
| Stability in Water | √ | √ |
| Transport (Fugacity) | –/* | √ |
| Biodegradation | –/* | √ |
| **ECOTOXICITY** | | |
| Acute Toxicity to Fish | –/* | √ |
| Acute Toxicity to Invertebrates | –/* | √/** |
| Acute Toxicity to Aquatic Plants | –/* | √/** |
| **MAMMALIAN TOXICITY** | | |
| Acute Toxicity | √ | √ |
| Repeated Dose Toxicity | √ | ### |
| Developmental Toxicity | √ | ### |
| Reproductive Toxicity | √/* | ### |
| Genetic Toxicity Gene Mutations | √ | √ |
| Genetic Toxicity Chromosomal Aberrations | √ | ### |

√ = Data are available and considered adequate.
√/* = Data available on reproductive organs in a repeated dose study.
√/** = Modeled data are available, but no empirical data are available.
– = No data available, or available data considered inadequate.
/* = No studies were available; however, we expect similar results to BHMT.
### = No studies were available; however, we expect similar results to crude BHMT.

**Evaluation of Data**

The available adequate data were broken out by discipline (physical chemical, environmental fate, ecotoxicology, and mammalian toxicology).

Crude BHMT and BHMT have similar physical chemical properties due to BHMT being a major component for crude BHMT. Available data (Table 2) correlate well and validate the proposal to use the BHMT data to aid in evaluation of crude BHMT toxicity.

**Table 2: Physical and Chemical Characteristics**

| | Crude BHMT | BHMT |
|---|---|---|
| **Physical Appearance** | Brown viscous semi-liquid or paste | White to slight yellow solid, shipped in bulk as a warm liquid |
| **Water Solubility** | 1% | 10.8 g/L (Estimated) |
| **Melting Point** | 32-34°C | 33-36°C |
| **Boiling Point** | Circa 249°C @ 100 mm Hg | 220°C @ 20 mm Hg |
| **Vapor Pressure** | 7 mm Hg @ 180°C | 82.5 mm Hg @ 250°C |
| **Density/ Specific Gravity** | 0.93-0.97 (Specific gravity) | No Data |
| **Octanol-Water Partition Coefficient (Log Kow)** | No Data | 1.8 (Estimated) (base form) |

Crude BHMT is a brown viscous liquid/semi-solid with an ammonia-like odor. Crude BHMT melts at 32-34°C, has a listed boiling point of 249°C, specific gravity of 0.93-0.97, water solubility of 1%, and a listed vapor pressure of 7 mm Hg at 180°C. BHMT has similar properties, in that it melts at 33-36°C, has a boiling point of 220°C, and vapor pressure of 82.5 mm Hg at 250°C.

Data on environmental fate are not available for crude BHMT; however, limited data on BHMT are available. As a complex and variable mixture, crude BHMT cannot be modeled for environmental fate. Inspection of their chemical structures and a review of estimated physical-chemical properties and environmental-fate characteristics, based on output from EPIWIN 3.05 modeling software (Syracuse Research Corporation), indicate that the known components of crude BHMT do not exhibit a potential to be persistent and/or bioaccumulative in the environment. BHMT is rapidly biodegraded when tested following standard protocols. At environmental pH, it is expected to be fully ionized and show little tendency for bioaccumulation. Based on Level III fugacity modeling using a standard emission scenario, BHMT is expected to partition primarily into soil and water. Inspection of the chemical structure and application of chemical principles indicate that BHMT will not readily hydrolyze in water or be subject to aqueous photolysis.

**Table 3: Environmental Fate**

| | Crude BHMT | BHMT |
|---|---|---|
| **Bioaccumulation*** | No Data | BCF = 4.8 (base form only) |
| **Biodegradation** | No Data | Ready biodegradable |
| **Fugacity*** | No Data | (base form)<br>Air 0%<br>Water 25.2%<br>Soil 74.7%<br>Sediments 0.1% |
| * = Modeled data | | |

No data are available on the aquatic toxicity of crude BHMT. Data available indicate that BHMT is of moderate concern for toxicity to fish. ECOSAR modeling data are in agreement with the empirical data for fish. No empirical data for either crude BHMT or BHMT are available for invertebrates and algae. Therefore, short-term aquatic toxicity tests are proposed for *Daphnia magna* and *Selenastrum*.

**Table 4: Aquatic Toxicity**

| | Crude BHMT | BHMT |
|---|---|---|
| **Log Kow** | No Data | 1.8 (E) |
| **Toxicity to Fish** (48-hour $LC_{50}$ value) | No Data | 76 mg/L (N)<br>79.6 mg/L (E) |
| **Toxicity to Invertebrates** (48-hour $EC_{50}$ value) | No Data | 5.7 mg/L (E) |
| **Toxicity to Algae** (96-hour $EC_{50}$ value) | No Data | 10.1 mg/L (E) |
| E = estimated value, N = value based on nominal test concentrations | | |

Acute toxicity data indicates that crude and pure BHMT exhibit similar acute toxicity (Table 5). Crude BHMT was slightly toxic via the acute oral route with a reported acute lethal dose (ALD) in rats of 1500 mg/kg in one acute study and an $LD_{50}$ in rats of 450 mg/kg in another study. BHMT also has an ALD in rats of 1500 mg/kg. Crude BHMT was considered to be at worst moderately toxic via the acute route (ALD > 200 mg/kg). Crude BHMT is corrosive to skin and a severe eye irritant.

**Table 5: Acute Mammalian Toxicity**

| | Crude BHMT | BHMT |
|---|---|---|
| **Oral** | ALD = 1500 mg/kg<br>$LD_{50}$ = 450 mg/kg | ALD = 1500 mg/kg |
| **Inhalation $LC_{50}$** | 6-hour > vapor saturation at ambient temperature | No Data |
| **Dermal ALD** | > 200 mg/kg<br>> 126 and < 200 mg/kg | No Data |
| **Dermal Irritation** | Corrosive | No Data |
| **Eye Irritation** | Severe irritant | No Data |
| **Dermal Sensitization** | No Data | No Data |

A summary of available data on repeated dose, developmental, and reproductive toxicity is shown in Table 6. Crude BHMT has been tested in a 13-week oral gavage study in rats. In this study, mortality was observed in 1/15 males and 1/15 females in the high dose group (120 mg/kg/day) and 1/15 males at the mid-dose group (50 mg/kg/day, death not considered treatment-related). Other toxic effects observed during the study included respiratory rales, decreased body weights, reduced food consumption, and an increase in segmented neutrophils. The NOEL for this study was 50 mg/kg/day for both sexes. Crude BHMT was also studied in a 13-week inhalation study in rats. A NOEL was not determined for this study as the lowest concentration level (10 $mg/m^3$) exhibited lesions in the respiratory tract, with target organs of the nasal passages, trachea, and lungs. BHMT was also tested in a developmental toxicity study in rats at dose levels of 50, 100, and 250 mg/kg. BHMT did not produce fetal effects at dose levels lower than where maternal effects existed; therefore, it was not considered to be a specific developmental toxin. Although no reproductive toxicity tests were conducted on either compound, no effect on testes or ovary weights were observed in 13-week oral and 13-week inhalation toxicity studies in rats. No microscopic findings were observed in the reproductive organs (ovaries, testis, epididymis, uterus, and/or vagina) of the high-dose group in either study.

**Table 6: Repeated Dose, Developmental, and Reproductive Toxicity**

| | Crude BHMT | BHMT |
|---|---|---|
| **Repeated Dose Toxicity (NOAEL)** | NOEL = 50 mg/kg in a 13-week oral study<br>NOEL <10 mg/m$^3$ in a 13-week inhalation study | No Data |
| **Developmental Toxicity** | Not a developmental toxin | No Data |
| **Reproductive Toxicity** | No effect on reproductive organs in subchronic studies. | No Data |

Crude BHMT and BHMT were not mutagenic when tested in *Salmonella* and *E. coli*. Additionally, crude BHMT was negative in an *in vitro* hepatocyte DNA repair assay, negative in an *in vitro* CHO/HGPRT cell gene mutation assay, and negative in an *in vivo* bone marrow chromosome aberration study.

**Table 7: Genetic Toxicity**

| | Crude BHMT | BHMT |
|---|---|---|
| **Mutagenic Activity in Bacterial Systems** | Negative | Negative |
| **Chromosome Aberrations** | Negative | No Data |

Overall, the toxicologic database for crude BHMT is fairly robust. In areas where data gaps exist for crude BHMT, data for BHMT are available. Because BHMT is the primary component of crude BHMT, it is reasonable to conclude that the crude BHMT would behave similarly to BHMT in the areas where data gaps are evident for the crude material: log Kow, stability in water, fugacity, biodegradation, and acute toxicity to fish. While we expect crude BHMT to have similar toxicity values to the modeled data presented for BHMT for acute toxicity to invertebrates and algae, there is no empirical data available to support the modeled BHMT data. Therefore, acute aquatic toxicity tests are proposed for *Daphnia magna* and *Selenastrum* (see Table 8). A 48-hour static *Daphnia magna* toxicity test with crude BHMT following OECD Guideline 202 is recommended, as well as an acute toxicity test to algae with crude BHMT following OECD Guideline 201.

**Table 8: Proposed Test Plan**

| | Crude BHMT |
|---|---|
| Acute Toxicity to Invertebrates | + |
| Acute Toxicity to Aquatic Plants | + |
| + = Testing recommended. | |

Exposure Assessment for Crude BHMT – DuPont and Solutia

Crude BHMT is a co-product produced in the manufacture of hexamethylenediamine (HMD). Crude BHMT is sold to several customers for use as an asphalt anti-stripping agent, a chelating agent for water treatment, or a curing agent for epoxy resins. DuPont and Solutia practice Responsible Care and assess the ability of potential customers to safely handle crude BHMT prior to commencing a commercial relationship. The Product Stewardship System works with customers to understand their applications and any issues associated with PPE (personal protective equipment), safety equipment (safety showers, eyewash stations, ventilation needs, etc.), storage concerns, disposal requirements, and MSDS questions.

Crude BHMT is manufactured at three DuPont and one Solutia facilities. The potential for exposure is the greatest during truck loading for production and during equipment breaks for maintenance. The sites can have from 430 to 2000 personnel working (construction, contractor, and plant employees). The areas where the substance is manufactured will have 20 to 40 operators during normal operations and 60 people during a shutdown or major construction activity. Two of the 3 DuPont sites ship their substance to the third site or a toller to refine the crude BHMT. Solutia only sells the crude product directly from the one facility.

The sites and toller have effective safety, health, and environmental practices and procedures in addition to engineering controls, environmental controls, and personal protective equipment to control exposure. Adequate safety equipment, such as safety showers, eyewash fountains, and washing facilities, are available in the event of an occupational exposure. DuPont and Solutia assess the ability of a toller to manage the risk of exposure prior to signing a contract. The DuPont contract requires that any incidents must be reported to DuPont.

Individuals handling crude BHMT should wear safety glasses and impervious clothing to prevent any contact with this product, such as gloves, apron, boots, or whole bodysuit made from neoprene, as appropriate. When the possibility exists for eye and face contact due to splashing or spraying of material, individuals handling crude BHMT should wear coverall, chemical splash goggles, and face shield. This material does not have established exposure limits. The following DuPont recommendations are based on the fact that similar amines typically have exposure limits of 1 to 10 ppm. Half-face air-purifying respirators should be used where airborne concentrations range up to 10 ppm. Full-face air-purifying respirators should be used where airborne concentrations range between 10 and 50 ppm. A positive-pressure air-supplied respirator should be used where airborne concentrations are expected to exceed 50 ppm. Final

determination of appropriate respiratory protection equipment should be made by a qualified safety or industrial hygiene professional. If there is potential contact with hot/molten material, wear heat resistant clothing and footwear.

No occupational exposure limits have been established. Air monitoring has not been conducted on crude BHMT.